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QUARTERMASTER RESEARCH & ENGINEERING COMMAND

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RADIATION CHEMISTRY LABORATORY SERIES

RESEARCH REPORT NO. 5

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers: Degassing

QUARTERMASTER RESEARCH & ENGINEERING CENTER

PIONEERING RESEARCH DIVISION

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FOREWORD

This report, which is No. 5 on Irradiation "Factor-Dependency" of the Radiation Chemistry Laboratory Series, deals primarily with the effect of degassing on the irradiation-induced polymerization of monomer systems.

Report No. 1, Styrene, gave data on the significance of factors such as: (1) atmosphere, (2) degassing, (3) diluent, (4) dose, (5) dose rate, (6) moisture, and (7) temperature on irradiation-induced polymerization and a statistical evaluation of atmosphere, dose rate, and temperature.

Report No. 2, Some Vinyl Monomers, gave results indicating that under the conditions employed: (1) polymerization rate is not equal to $kI^{1/2}$, (2) the E-value ("G_e"-value) decreases with an increase in dose rate, (3) there is non-additivity of dose, and (4) unless parameters are critically defined, the formulation of rate has no significance.

Report No. 3, Styrene with Additives, provided data from which it was concluded that: (1) the effect of an additive is a function of dose rate with respect to molecular weight and yield, (2) the molecular weight decreases with an increase in dose rate for all additives used, (3) an inverse ratio is apparent with respect to molecular weight and yield, (4) an additive, as a function of dose rate, may either decrease or increase the yield, and (5) the efficiency of polymerization decreases markedly at the higher dose rates.

From Report No. 4, Irradiation Cycle, it was concluded that: (1) something more than a three-minute cycle at 75°C is the most efficient, (2) the relative efficiency of a time cycle over continuous irradiation decreases with an increase in dose rate, (3) efficiency decreases markedly at the higher dose rates, (4) previous reaction rate formulations are not applicable, and (5) the most desirable time cycle and temperature is a function of the monomer system.

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By Ed. F. Degering, G. J. Caldarella, Flora E. Evans,
and Stephen Grib

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A. Introduction

The experimental results reported herein and heretofore represent relative rather than absolute values. This is a consequence of certain slight uncontrollable variations in parameters, which were considered in some detail in Section A of both Research Report No. 3 and No. 4 of the Radiation Chemistry Laboratory Series.

In exploratory studies on irradiation-induced polymerization, there was an indication that degassing of the monomer, prior to sealing off in the reaction tube, might be an important parameter. An experiment was planned, accordingly, for the evaluation of the effect of a single degassing and vacuum or argon on the polymerization of monomer systems by continuous irradiation at 25°C and intermittent irradiation on a 30-minute cycle at a temperature of 75°C.

B. Preparation of Samples

In this particular study ten samples were prepared for each of the monomer systems: acrylonitrile, butyl acrylate, styrene, vinyl acetate, acrylonitrile-styrene (1/1 mixture by volume), butyl acrylate-styrene (1/1), and vinyl acetate-styrene (1/1). Thirty additional samples were prepared of acrylonitrile of which half were degassed by freezing with a slurry of acetone, and six samples of vinyl acetate and fourteen samples of styrene were similarly prepared.

1
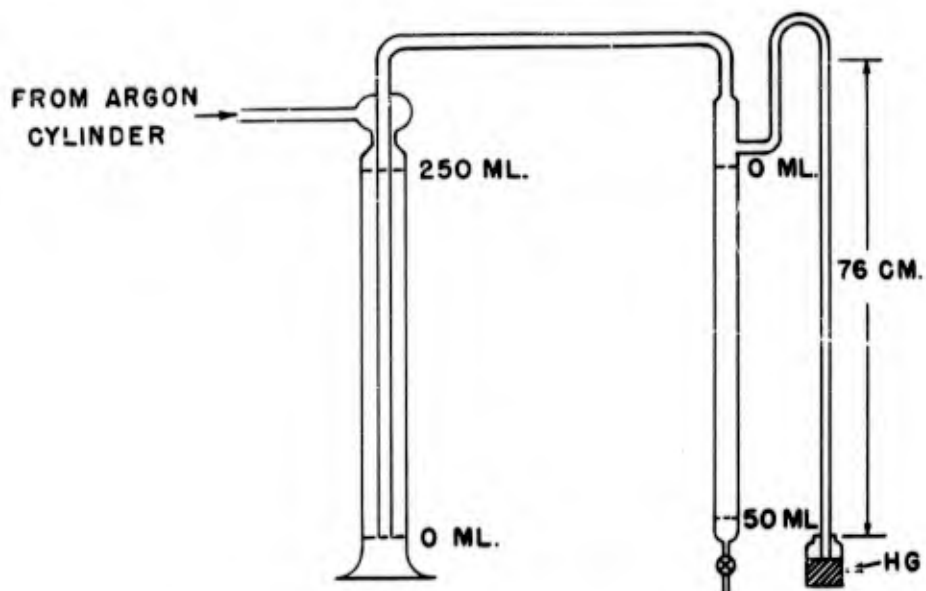
Figure 1. Apparatus for measuring out samples of monomer in the presence of argon with slow flow of argon through the system to exclude both air and moisture.
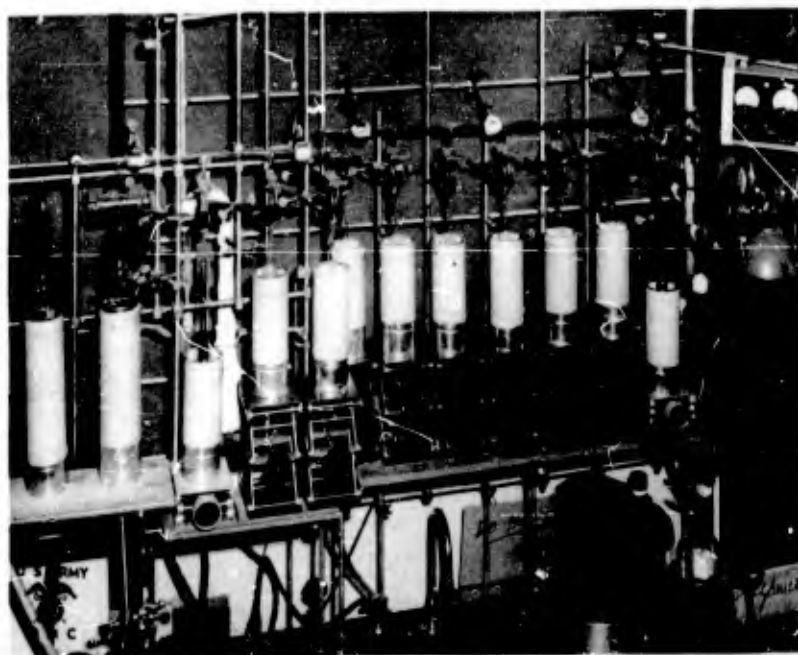
Figure 2. Apparatus used in preparation of samples.

Figure 3. Acrylonitrile (D-708-A): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed. The 3- and 5-triplet bars were calculated from the 1-triplet bar by use of the reaction rate formulation, $kI^{0.7}$.

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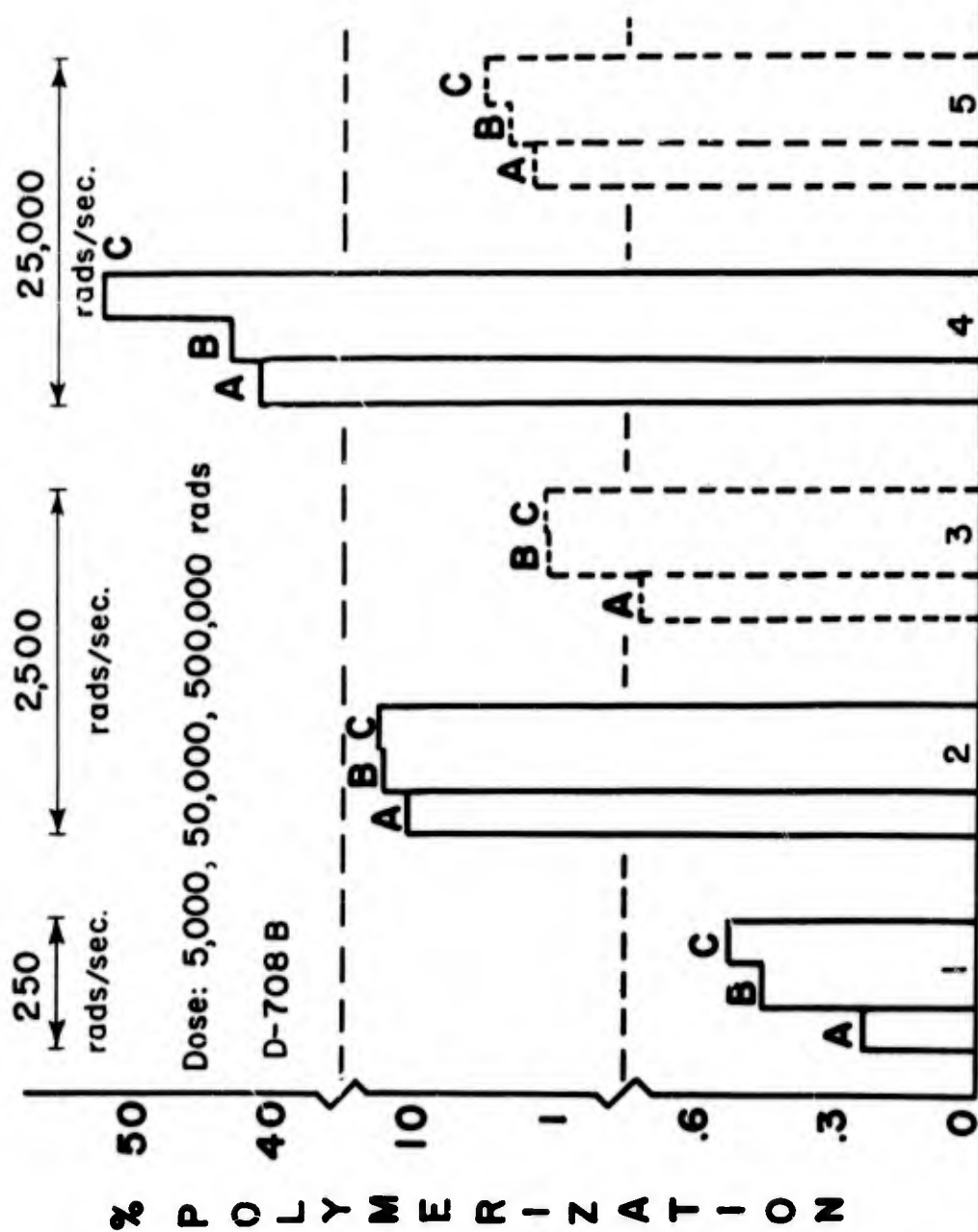
Figure 4. Butyl Acrylate (D-708-B): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed. The 3- and 5-triplet bars were calculated from the 1-triplet bar by use of the reaction rate formulation, $kI^{1/2}$.

% POLYMERIZATION

50

40

10

1

.6

.3

0

D-708 B

Dose: 5,000, 50,000, 500,000 rads

250 rads/sec.

2,500 rads/sec.

25,000 rads/sec.

4

Figure 5. Styrene (D-708-D): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed. The 3- and 5-triplet bars were calculated from the 1-triplet bar by use of the reaction rate formulation, $kI^{1/2}$.
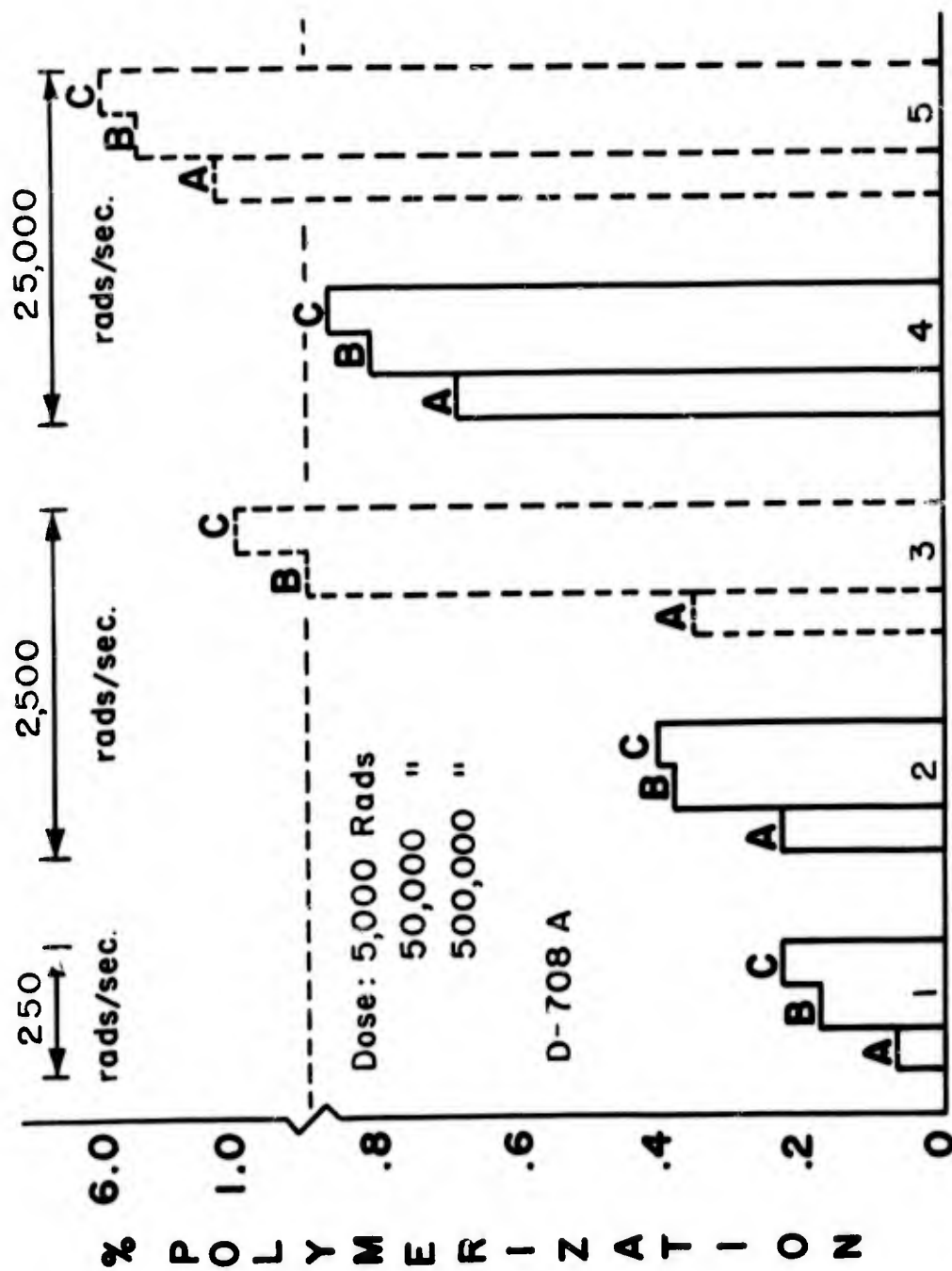
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Figure 6. Vinyl Acetate (D-708-C): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed. The 3- and 5-triplet bars were calculated from the 1-triplet bar by use of the reaction rate formulation, $kI^{1/2}$.
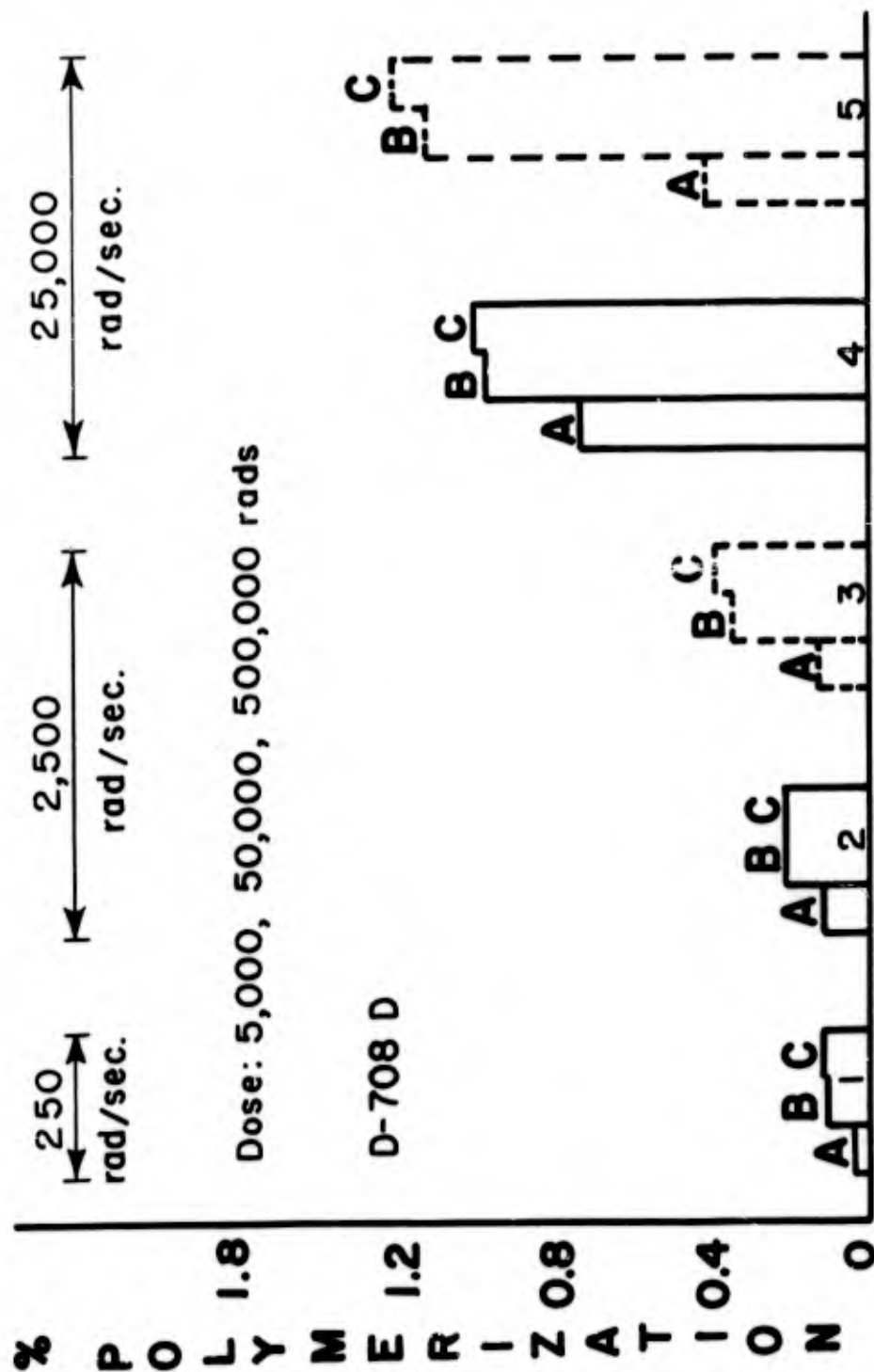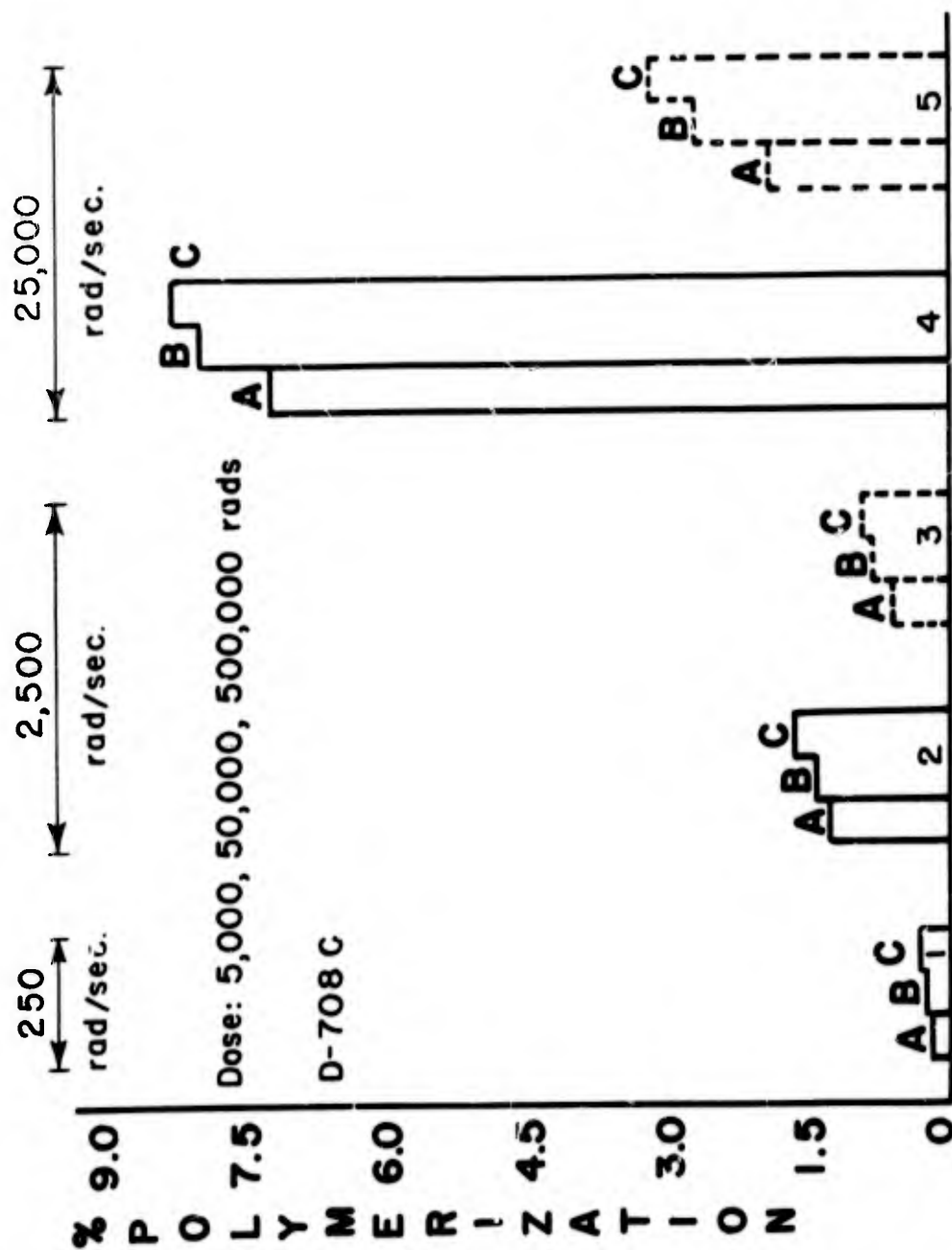
The procedure developed in this laboratory for the preparation of the monomer samples is as follows: The monomer is vacuum distilled, dried several days in a refrigerator over anhydrous potassium carbonate, and siphoned as used into a 250-ml. glass-stoppered graduate, which is connected in turn to an automatic burette through which a slow stream of argon flows. The burette is filled from the graduate by the use of slight argon pressure (Figure 1, page 2).

Ten 1 × 12-inch pyrex test tubes, equipped with ground glass male joints with a constriction in the tubing, are placed on the vacuum manifold (Figure 2, page 2), flamed out twice at 300 microns and once at 5 microns, and then filled with argon. A 20-ml. portion of the desired monomer is transferred from the burette to each of the argon-filled test tubes, which are replaced in turn on the manifold. Then Dewar flasks of liquid nitrogen are slowly raised by use of jacks in order to freeze the monomer.[1] The stopcocks to the manifold are opened one by one by a quarter turn and the tubes evacuated to about 300 microns with an auxiliary pump, which is connected to the right end of the manifold (Figure 2, page 2).[2] The auxiliary pump is closed off from the manifold, which is opened in turn to the high vacuum system at the left. The pressure in the system is reduced to 5 microns, the stopcocks closed by a quarter turn, the Dewar flasks lowered, and the monomer allowed to melt if degassing is desired.[3] The monomer is frozen again by raising the Dewar flasks, the stopcocks opened by a quarter turn, and the system again evacuated initially by

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[1] The level of the liquid nitrogen should be kept below the liquid-solid interface (except for the initial half inch) until solidification has occurred in order to minimize breakage of the tubes.

[2] The auxiliary pump is used to avoid contamination of the high vacuum system, particularly in case of a broken tube.

[3] Samples which were not degassed were sealed off after freezing.

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Figure 7. Acrylonitrile-Styrene (1/1 mixture, D-708-E): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed.

Figure 8. Butyl Acrylate-Styrene (1/1 mixture, D-708-F): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed.

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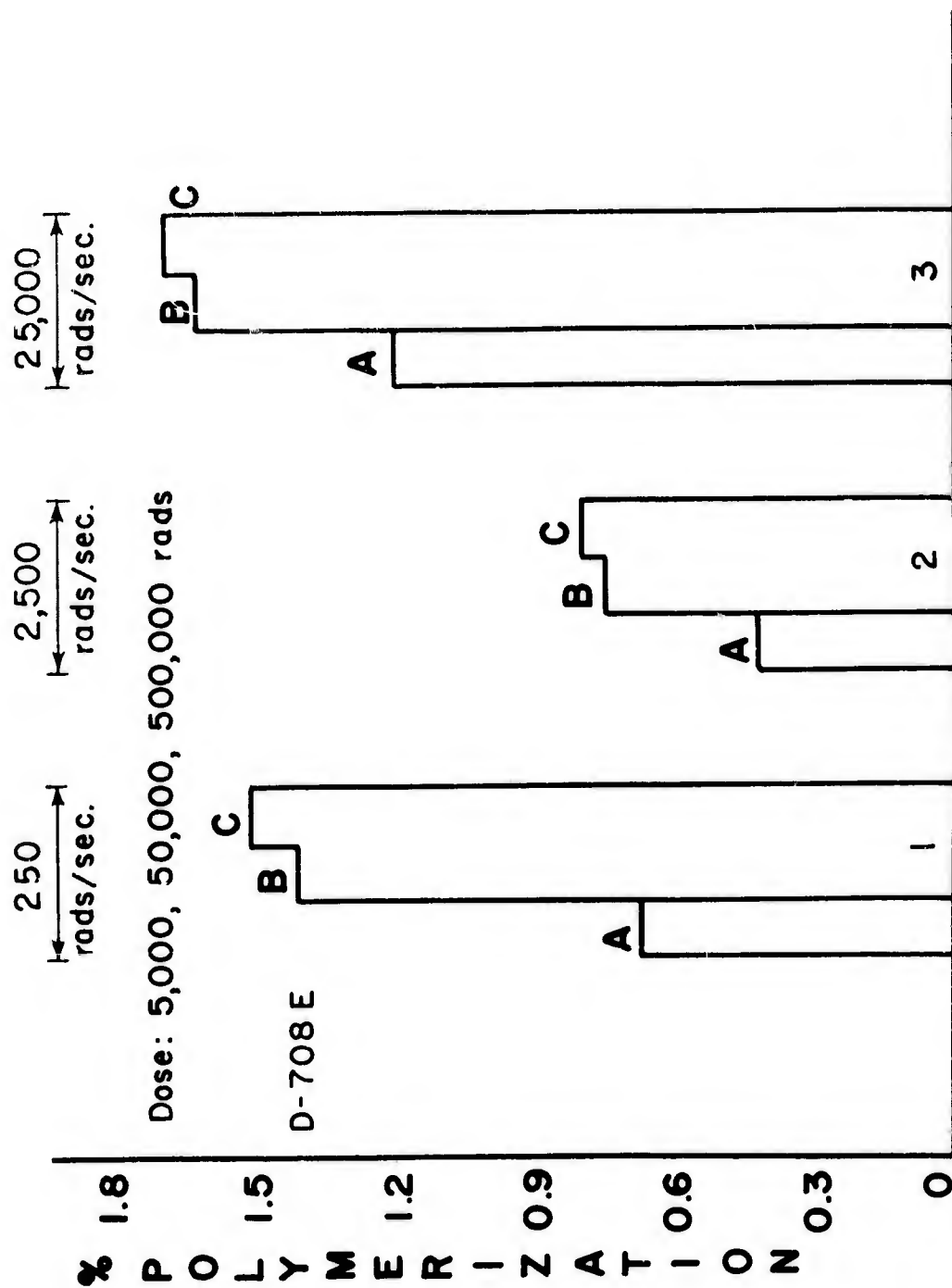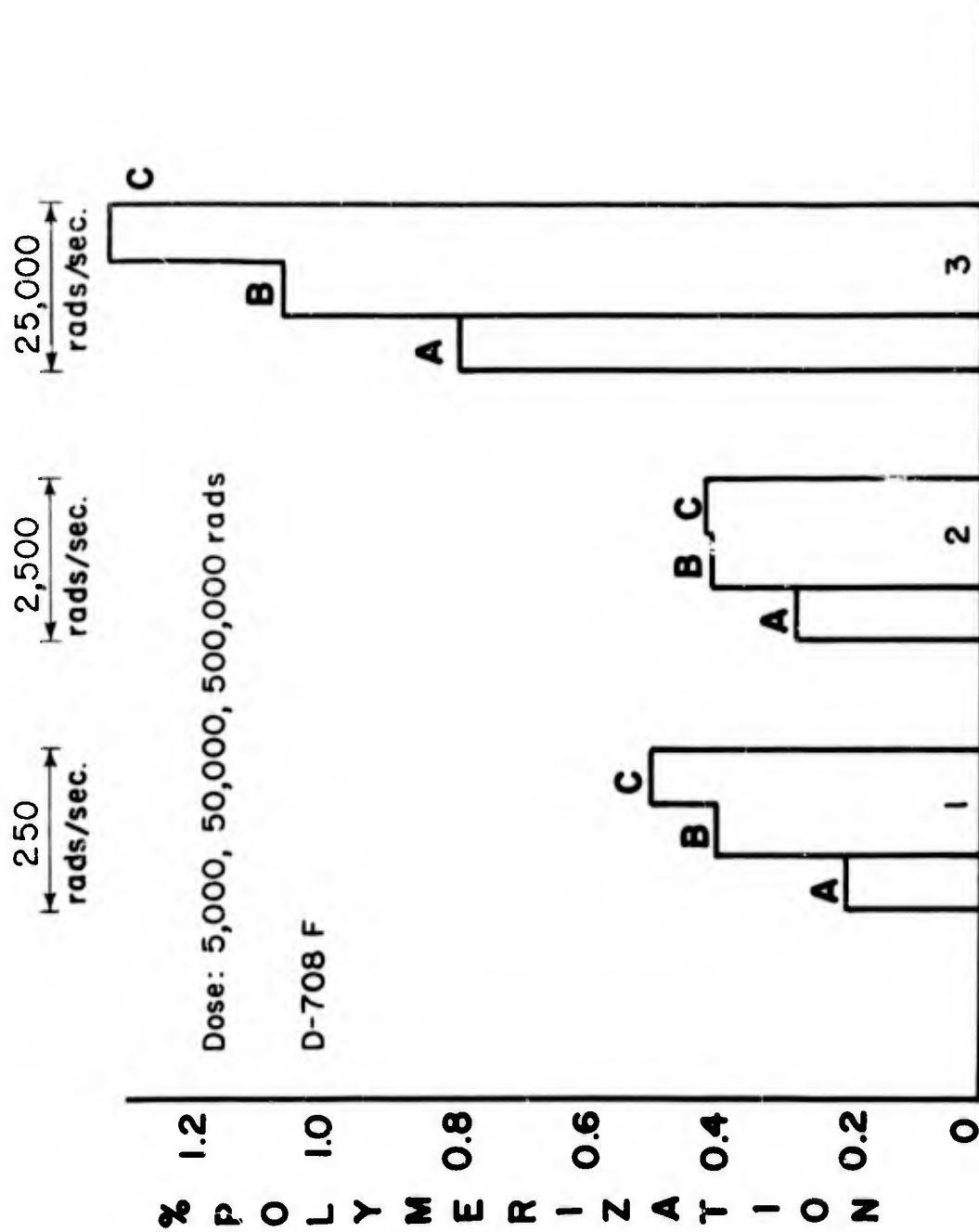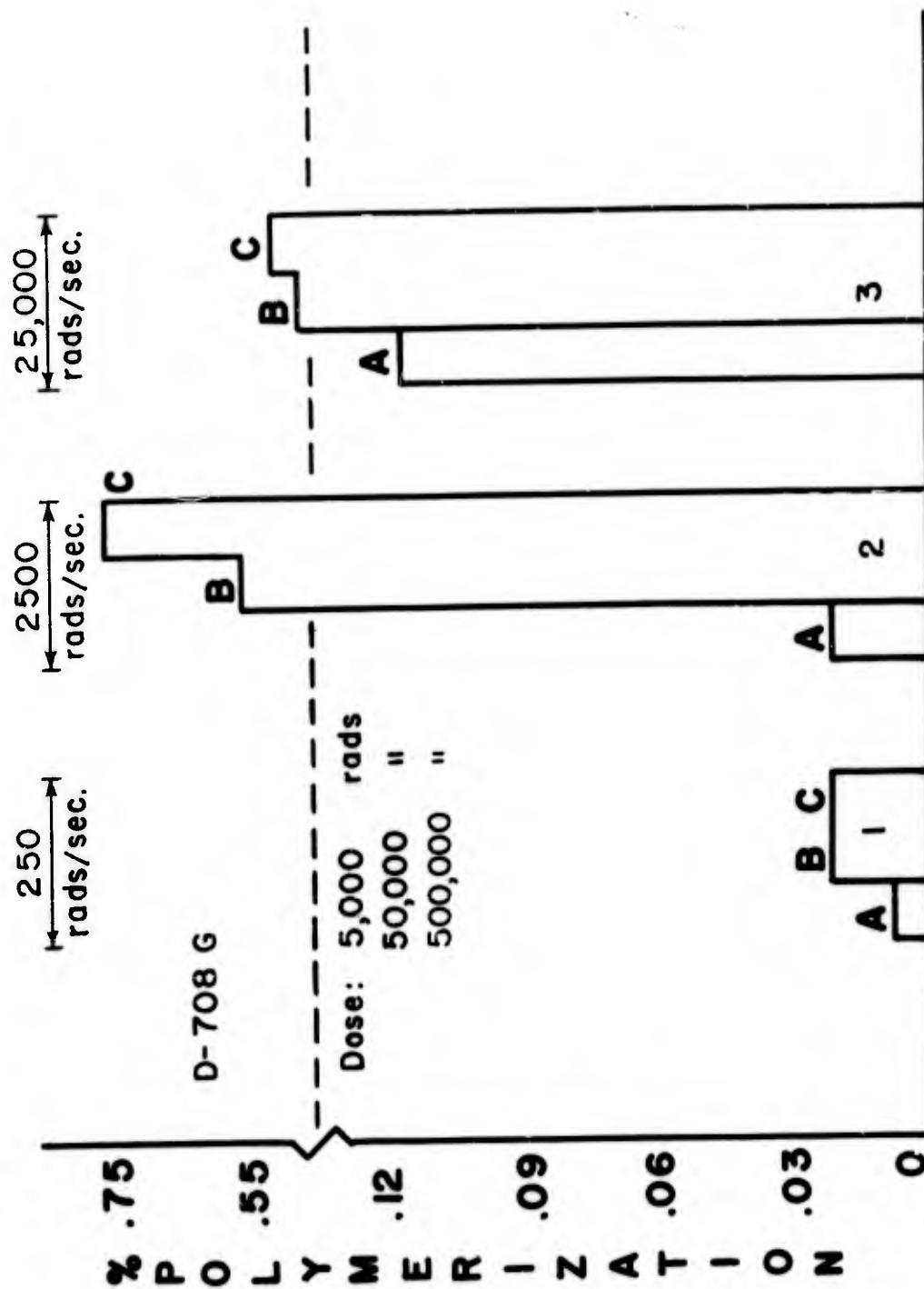Figure 9. Vinyl Acetate-Styrene (1/1 mixture, D-708-G): Samples for the B- and C-bars were degassed once, whereas those for the A-bars were not degassed.

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use of the auxiliary pump and subsequently by the high vacuum system. The pressure is reduced once again to 5 microns, the stopcocks closed by a quarter turn,[4] and the tubes sealed off and stored at -20°C until all of the samples are ready for packaging for irradiation. The tubes are then strip-packaged in polyethylene for convenience in handling, according to scheduled dose rate, and returned to storage at -20°C until time for irradiation.

The samples for graphs 11, 12, 14, and 15, however, were not sealed off under vacuum. Instead, these tubes were filled with argon to give a pressure of about 630 mm. of mercury. In order to do this safely without causing liquefaction of the argon, the freezing agent employed was a slurry of acetone at approximately -95°C.

C. Irradiation of Samples

The samples for Figures 3 to 10 were exposed to continuous irradiation with a resonant transformer at a distance of about two feet from the beam window.

The samples for Figures 11 to 15 were placed, according to scheduled dose rate, in 1×1.5-foot aluminum trays, heated one-half hour at 75°C in a precision oven, irradiated at the scheduled dose rate, returned to the oven for 30 minutes, and then given comparable irradiation and heating until five cycles were completed. The aluminum trays were insulated, to minimize temperature changes, from the conveyer by one inch of polystyrene foam.

After irradiation, the samples were returned to storage at -20°C until the tubes were opened for the processing of the irradiated product.

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[4] To maintain the vacuum at 5 microns while the stopcocks are being closed, only one-quarter of a turn of the stopcock should be used inasmuch as there is a very slow distillation of the volatiles from the apiezon grease into the vacuum cups.
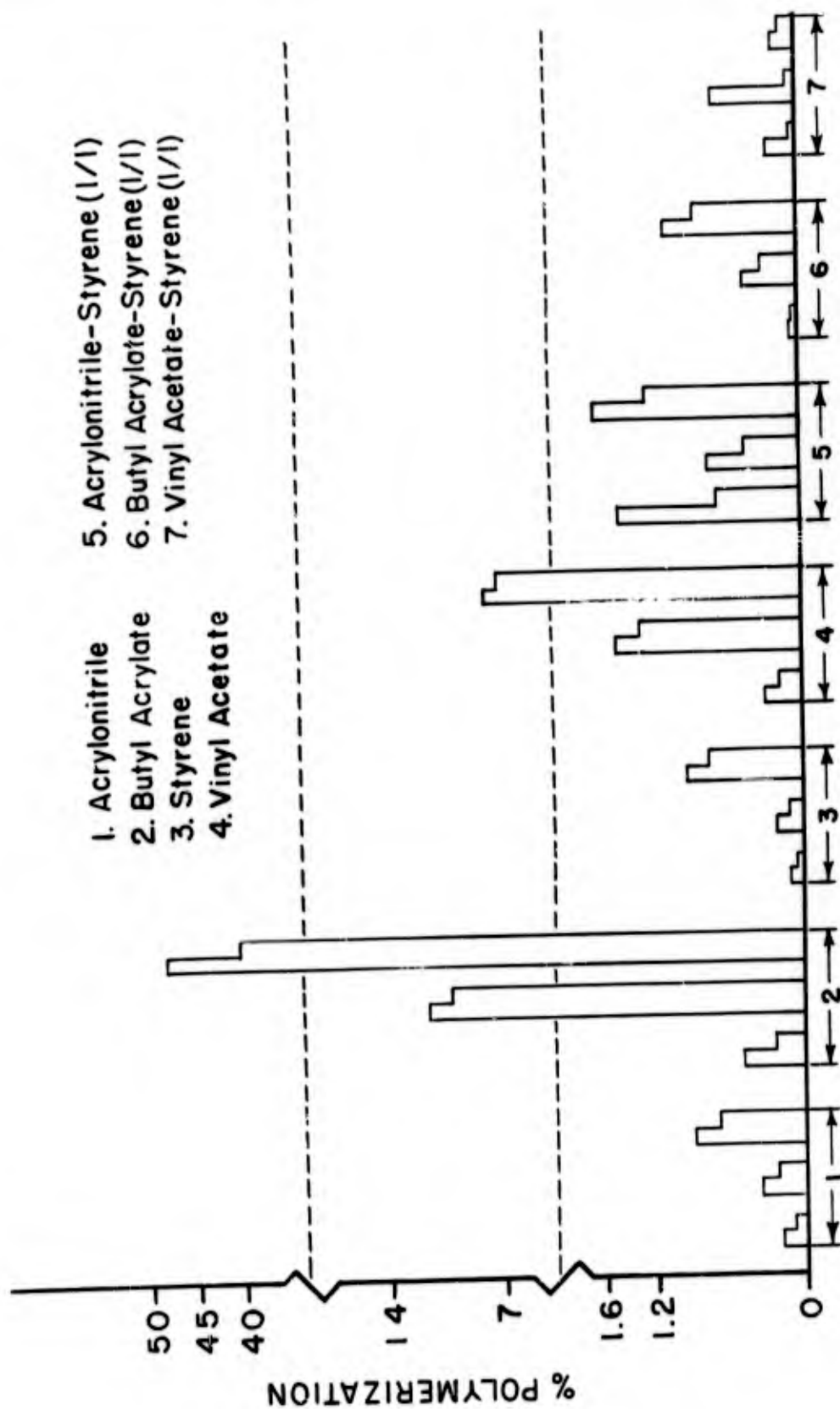
Figure 10. Composite of Figures 3 to 9, in which the left member of each twin bar was degassed whereas the right member was not degassed.

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D. Processing of Samples

The procedure developed by the Radiation Chemistry Laboratory for the processing of irradiated monomer systems is discussed in some detail in Research Report No. 3, Section D, page 13, dated November 1960, and in Research Report No. 4, Section D, page 7, dated December 1960.

E. Experimental Results

Bar-graphs of Figures 3 to 10 (pages 3, 4, 5, 6, 8, 9, 10, and 12) represent percentages of polymerization obtained by the irradiation of acrylonitrile, butyl acrylate, styrene, vinyl acetate, acrylonitrile-styrene (1/1 mixture by volume), butyl acrylate-styrene (1/1), and vinyl acetate-styrene (1/1) by continuous electron bombardment with a 2 Mev resonant transformer. Dose rates of 250, 2,500, and 25,000 rads per second were used with corresponding total doses of 5,000, 50,000 and 500,000 rads.

The experimental results for acrylonitrile, butyl acrylate, styrene, and vinyl acetate are given by the bar-graphs of Figures 3 to 6 (pages 3 to 6). The samples for the A-bar of each triplet were not degassed, whereas the B- and C-bars give data from samples which were subjected to one degassing at 5 microns. Samples for the No. 1-bars were irradiated at a dose rate of 250 rads per second, those for the No. 2-bars at 2,500 rads per second, and those for the No. 4-bars at 25,000 rads per second. The samples for the No. 1-bars in each bar-graph had a dose of 5,000 rads, those for the No. 2-bars 50,000 rads, and those for the No. 4-bars 500,000 rads. The No. 3- and 5-bars in each of these graphs represent values which were calculated from the No. 1-bars by use of the formulations: reaction rate = $kI^{0.7}$ for acrylonitrile, and reaction rate = $kI^{1/2}$ for the other three monomers. In Figures 3 and 5 (pages 3 and 5) the observed values are less than the calculated values, whereas in Figures 4 and 6 (pages 4 and 6) the reverse is true. In each of these systems the observed results do not conform to the values derived by use of the conventional formulations. This
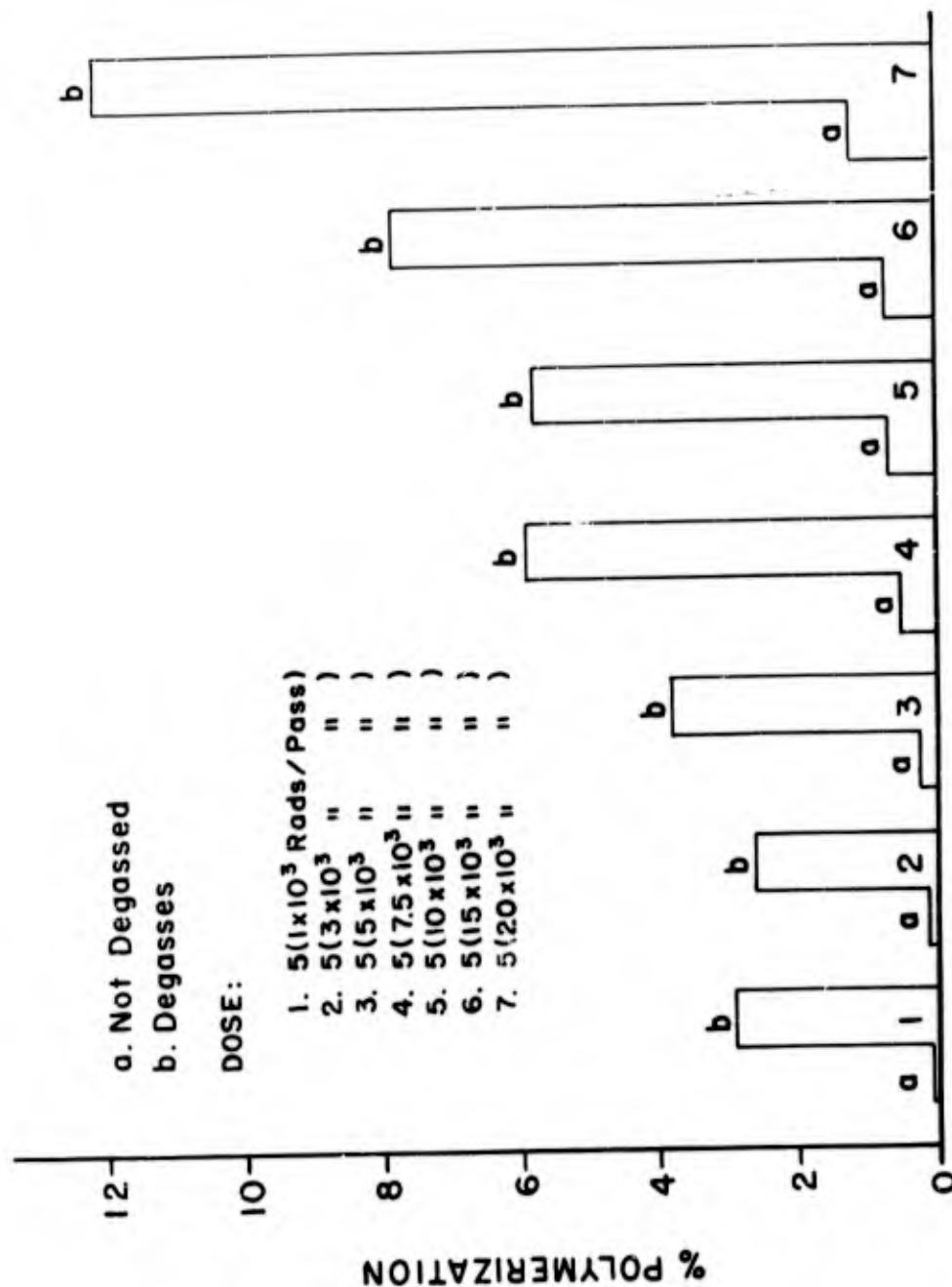
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Figure 11. Acrylonitrile (D-673): Samples for the a-bars were not degassed, whereas those for the b-bars were frozen with a slurry of acetone and evacuated to 5 microns, stopcocks closed, samples allowed to melt and degass, then frozen again and evacuated to 5 microns, argon introduced to a pressure of 630 mm. and the samples sealed off and irradiated as indicated.
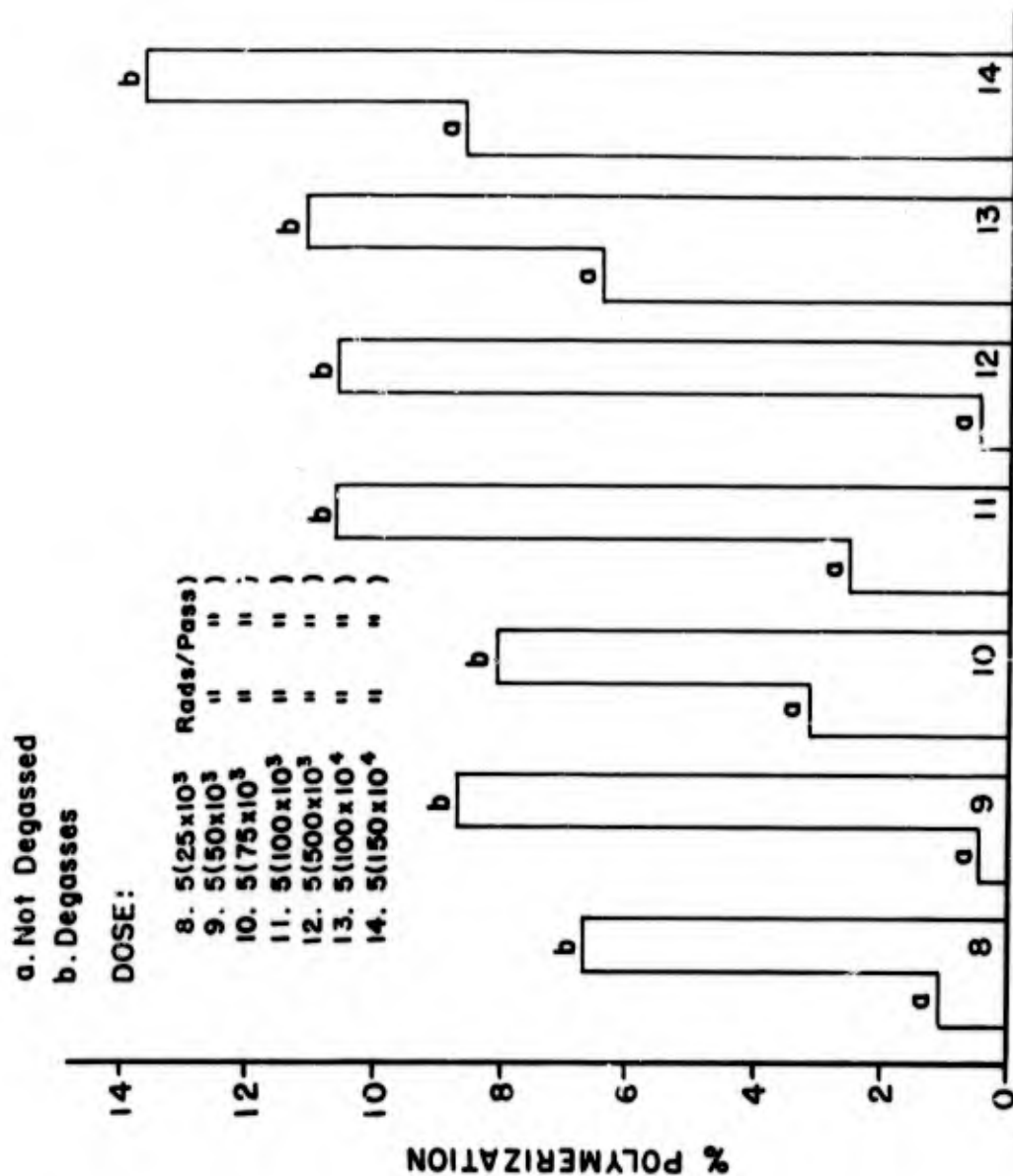
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Figure 12. Acrylonitrile (D-673): Samples for the a-bars were not degassed, whereas those for the b-bars were frozen with a slurry of acetone and evacuated to 5 microns, stopcocks closed, samples allowed to melt and degass, then frozen again and evacuated to 5 microns, argon introduced to a pressure of 630 mm. and the samples sealed off and irradiated as indicated.
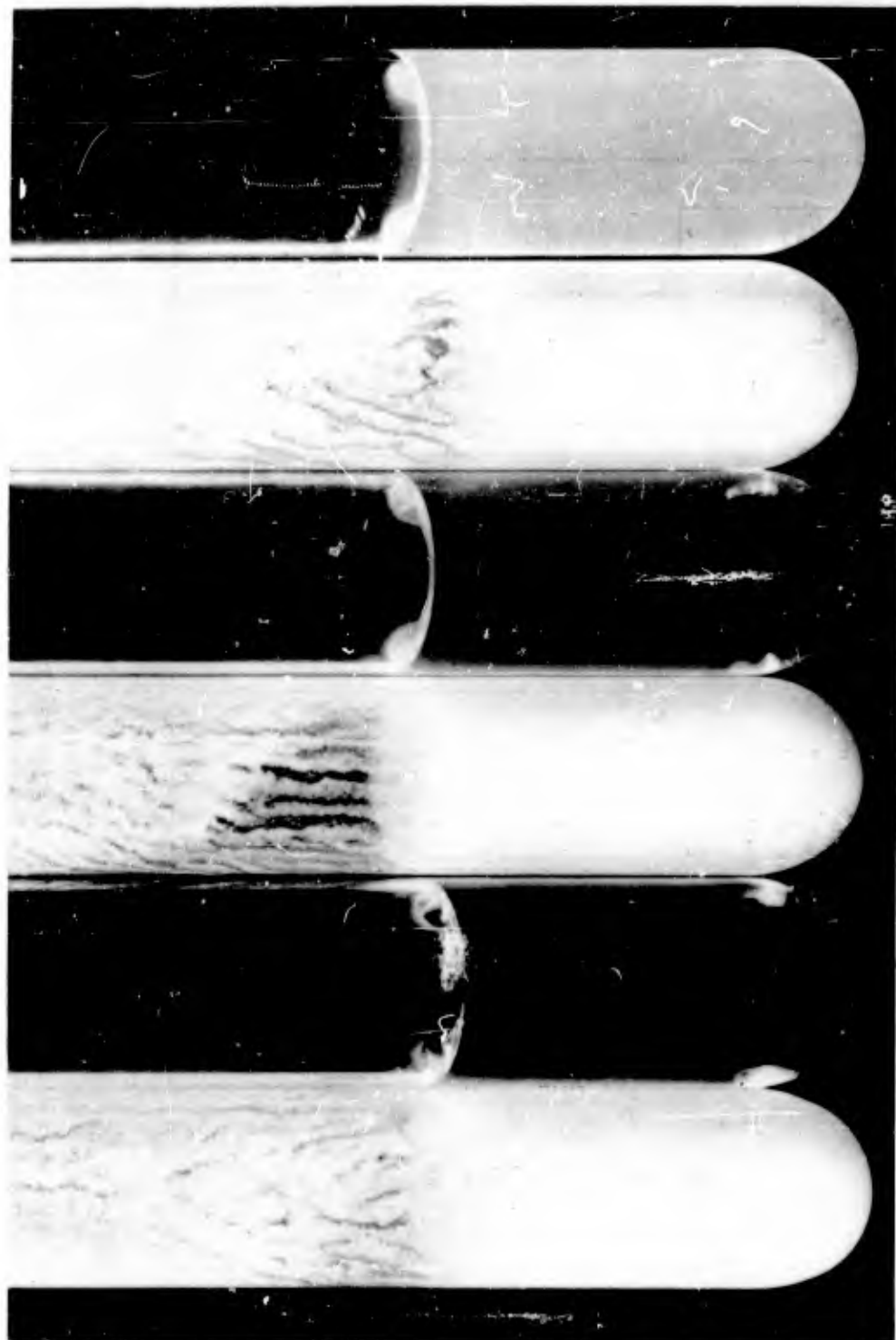
Figure 13. Acrylonitrile (D-673): Left to right, three sets of duplicates, except the samples for tubes 1, 3, and 5 were degassed once only. All received five exposures at: left pair, 1,000 rads per pass; center pair, 3,000 rads per pass; and right pair, 5,000 rads per pass, all on a 30-minute cycle at 75°C.

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is not altogether unexpected inasmuch as these formulations were derived under vastly different experimental conditions.

The B- and C-bars are consistently higher than are the corresponding A-bars, but the spread between the A- and the BC-bars varies with the monomer system. The greatest difference is observed for acrylonitrile, with varying differences for the other three monomer systems. Stated otherwise, the sensitivity of the degassing effect depends on the monomer system, but in each of the seven monomers of this study the effect was positive.

The bar-graphs of Figures 7 to 9 (pages 8 to 10) record comparable results for the acrylonitrile-styrene, the butyl acrylate-styrene, and the vinyl acetate-styrene mixtures. The A-bars, as noted previously, are for data obtained from non-degassed samples, whereas the B- and C-bars deal with samples which were degassed once at 5 microns. Consistently, the A-bars represent smaller values than do the corresponding B- and C-bars. Although the differences are small in some of the bar-triplets, the pattern is nonetheless consistent.

The composite results for the degassing effect for seven monomer systems at three dose rates are given in Figure 10 (page 12). The left bar of each bar-pair represents the percent of polymer obtained from a sample which had been degassed once only, whereas the right bar of each bar-pair indicates the yield obtained from a comparable non-degassed sample. The left member of each triplet set is for data obtained at 250 rads per second and a dose of 5,000 rads, the center member is for 2,500 rads per second and a dose of 50,000 rads, and the right member is for a dose rate of 25,000 rads per second and a dose of 500,000 rads. It is apparent from the graph that all of the degassed samples yielded more polymer than did the corresponding samples which were not degassed. The relative effectiveness of the degassing, moreover, appears to be a function of both the dose rate and the monomer system.

The results obtained from sixteen samples of acrylonitrile, half of which were degassed once only, are presented
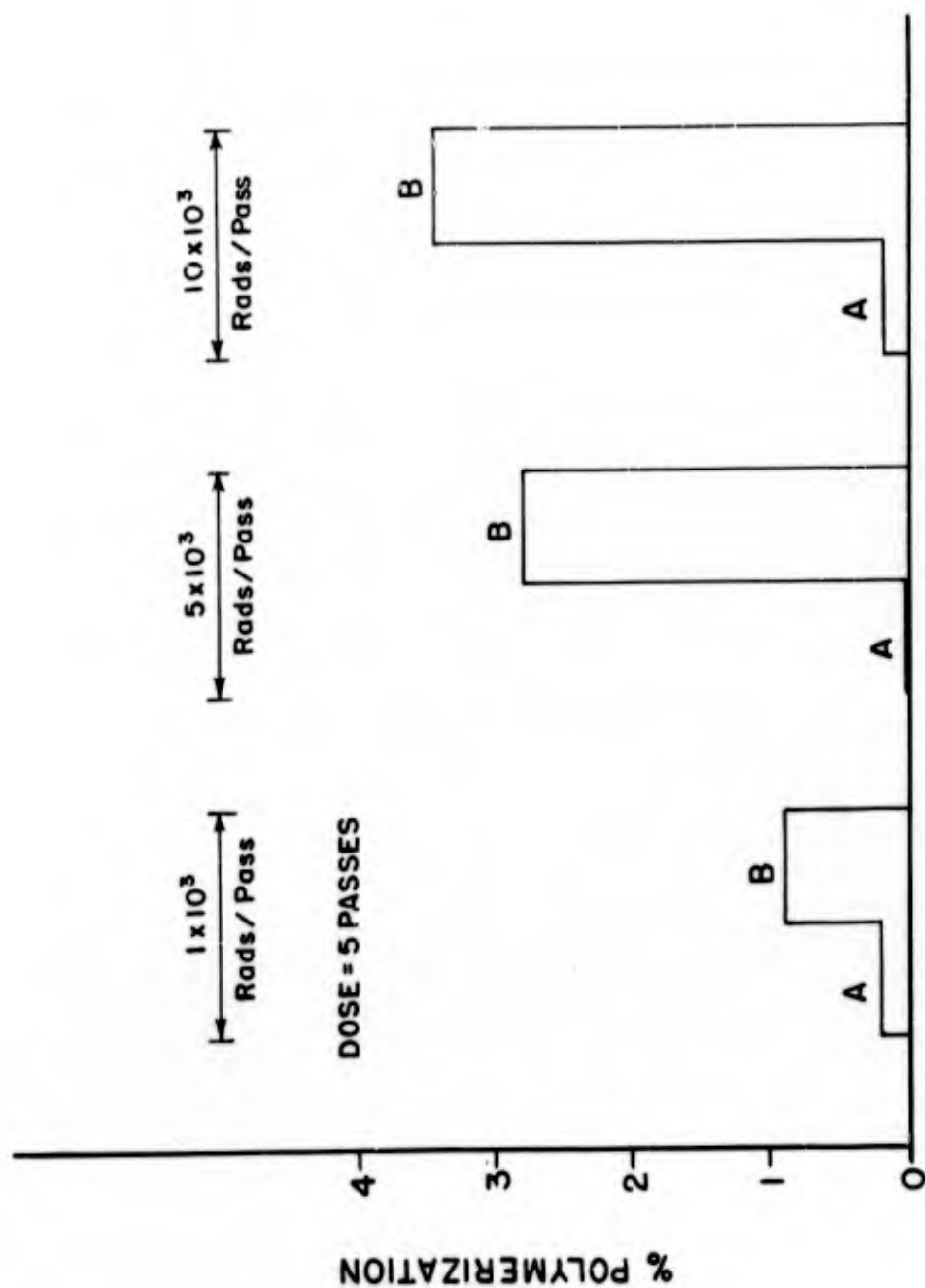
17

Figure 14. Vinyl Acetate (D-672): The samples for the B-bars were degassed as in Figures 13 and 14, whereas those for the A-bars were not degassed. Irradiated under argon at a pressure of 630 mm. of mercury.

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in Figure 11 (page 14). These samples for Figure 11 were irradiated at 75°C at seven dose rates, ranging from 1,000 rads per exposure to 20,000 rads. The total dose in each case was five times the dose rate indicated on the graph.

The samples for the b-data at each dose rate were degassed once only at about 10 microns, whereas the corresponding samples for the a-data were not degassed. There is a consistent pattern in this series over the seven dose rates used, with the b/a-ratio, that is the ratio of the product from the degassed to the non-degassed samples being 290/1 at 1,000 rads per exposure, 22/1 at 3,000, 16/1 at 5,000, 11/1 at 7,500, 8/1 at 10,000, 11/1 at 15,000, and 10/1 at 20,000 rads per exposure. There is, in general, a decrease in the b/a-ratio with an increase in dose rate. These data represent single point determinations, but the over-all pattern is evident. The heat control samples gave less than 0.01% polymerization for a comparable heating cycle at 75°C.

The data obtained from a comparable series, which were irradiated at dose rates ranging from 25,000 rads per exposure to 1,500,000 are shown as Figure 12 (page 15). Each of the samples received five exposures on a 30-minute irradiation cycle at 75°C. The pattern of the b/a-ratio follows in general that of Figure 11 (page 14), but with a more significant decrease in the ratio with an increase in dose rate and total dose. At 25,000 rads per exposure the b/a-ratio, that is the amount of product obtained from the degassed sample to the corresponding sample which was not degassed, is 5/1, at 50,000 rads it is 4/1, at 75,000 rads it is 3/1, at 100,000 rads it is 4/1, at 500,000 rads it is 2/1, at 1,000,000 rads it is 1.8/1, and at 1,500,000 rads per pass under the beam the b/a-ratio is only 1.6/1. The quotient from the b/a-ratio at 1,000 rads per exposure to that obtained at 1,500,000 rads per pass is 181/1. Stated otherwise, the single degassing used in this study contributes 181 times as much to polymer formation at the lowest dose rate used as it does at the highest dose rate. This is another marked confirmation of the relative efficiency of irradiation-induced polymerization at low dose rates.
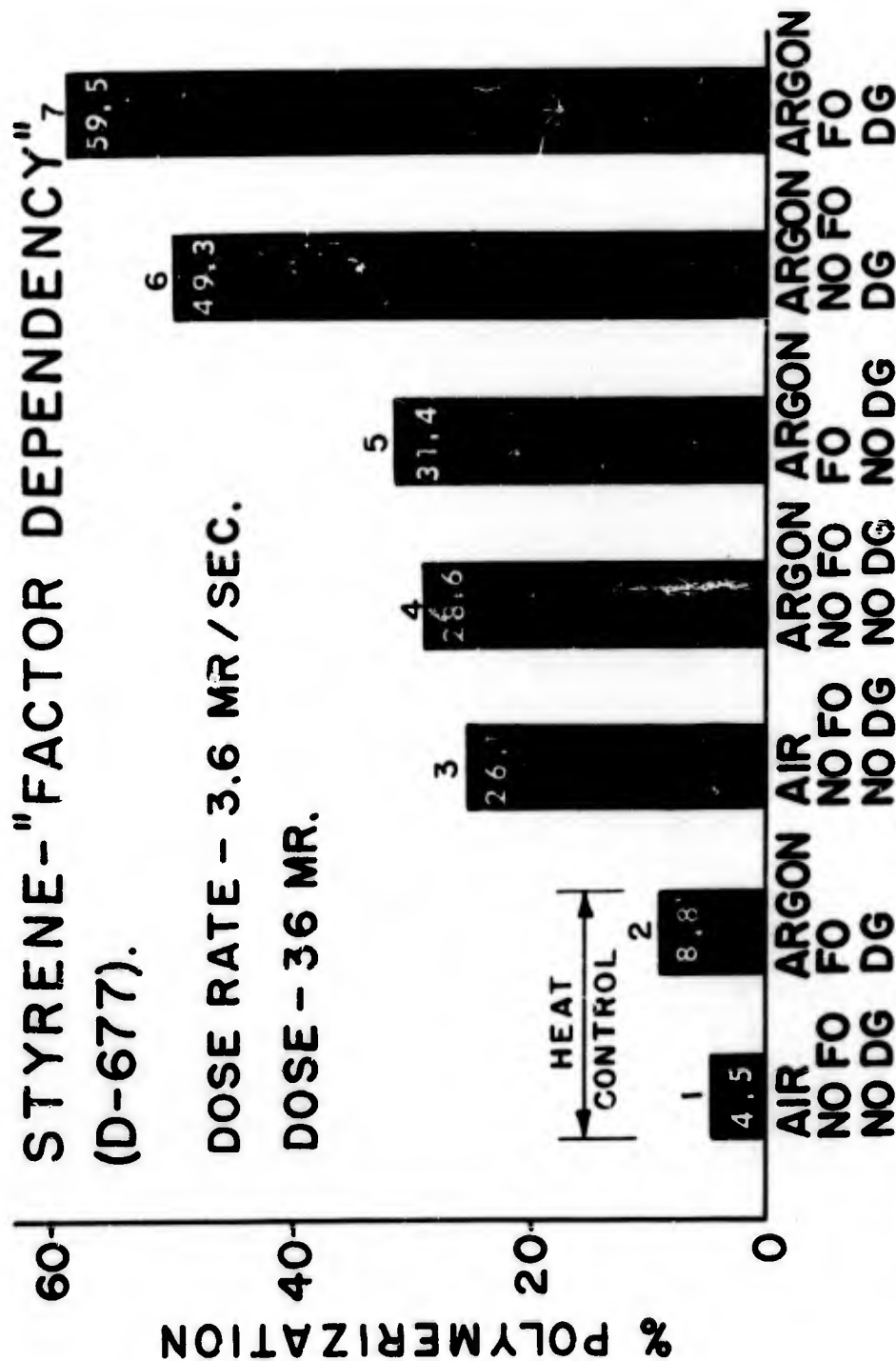
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Figure 15. Styrene (D-677): Effect of degassing as a function of atmosphere and flame-out of the irradiation tubes. The degassing was as in the samples for Figures 11 and 12.

In a degassing study on vinyl acetate at three dose rates, the samples were sealed off in the presence of argon at a pressure of about 630 mm. of mercury. The results are recorded as Figure 14 (page 18). The degassed samples yielded significantly more polymer at all three dose rates and dose levels. As in the case of acrylonitrile of Figures 11, 12, and 13 (pages 14 to 16), the presence of argon appears to contribute to the effectiveness of degassing with respect to polymer formation.

The results obtained from the irradiation of styrene under five experimental conditions are shown as Figure 15 (page 20). On the basis of these results one may conclude that the irradiation-induced polymerization of styrene under these conditions is improved in turn by: (1) replacing air by argon, (2) flame-out of the tubes, (3) degassing, and (4) a combination of flame-out and degassing in the presence of argon. The latter combination, that is, flame-out, degassing, and then filling the tube with argon before sealing off and irradiating, yields about 2.1 times as much polymer under these specific conditions as is obtained in the absence of flame-out and degassing. Note that the dose rate was 3.6 megarads per second for a total of ten exposures.

F. Summary

From the results obtained in these studies one may conclude that:

1. Degassing may significantly increase the yield of polymer obtained by irradiation-induced polymerization.

2. The relative significance of degassing is a function of: (a) the monomer system, (b) the dose rate, and (c) the presence of argon.

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G. Acknowledgements

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